

We claim:-

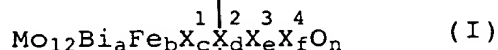
1. a process for the catalytic gas-phase oxidation of propene to acrylic acid, in which a reaction gas starting mixture 1  
5 which contains propene, molecular oxygen and at least one inert gas, comprising at least 20% by volume of molecular nitrogen, and which contains the molecular oxygen and the propene in a molar  $O_2:C_3H_6$  ratio of  $\geq 1$  is first passed, in a  
10 first reaction stage at elevated temperatures, over a first fixed-bed catalyst, whose active material is at least one multimetal oxide containing molybdenum and/or tungsten and bismuth, tellurium, antimony, tin and/or copper, in such a way that the propene conversion in a single pass is  $\geq 90$  mol%  
15 and the associated selectivity of the acrolein formation and of the acrylic acid byproduct formation together is  $\geq 90$  mol%, the temperature of the product gas mixture leaving the first reaction stage is, if required, reduced by indirect and/or direct cooling and, if required, molecular oxygen  
20 and/or inert gas are/is added to the product gas mixture, and the product gas mixture, as reaction gas starting mixture 2 which contains acrolein, molecular oxygen and at least one inert gas, comprising at least 20% by volume of molecular nitrogen, and which contains the molecular oxygen and the  
25 acrolein in a molar  $O_2:C_3H_4O$  ratio of  $\geq 0.5$ , is then passed, in a second reaction stage at elevated temperatures, over a second fixed-bed catalyst whose active material is at least one molybdenum- and vanadium-containing multimetal oxide, in such a way that the acrolein conversion in a single pass is  
30  $\geq 90$  mol% and the selectivity of the acrylic acid formation balanced over both reaction stages is  $\geq 80$  mol%, based on propene converted, wherein
  - a) the loading of the first fixed-bed catalyst with the  
35 propene contained in reaction gas starting mixture 1 is  $\geq 160$  l(S.T.P.) of propene/l of catalyst bed · h,
  - b) the first fixed-bed catalyst consists of a catalyst bed arranged in two spatially successive reaction zones A,B,  
40 the temperature of reaction zone A being from 300 to 390°C and the temperature of reaction zone B being from 305 to 420°C and at the same time at least 5°C above the temperature of reaction zone A,
  - c) the reaction gas starting mixture 1 flows first through  
45 reaction zone A and then through reaction zone B,

- d) the reaction zone A extends to a propene conversion of from 40 to 80 mol%,
- 5 e) the loading of the second fixed-bed catalyst with the acrolein contained in reaction gas starting mixture 2 is  $\geq 140$  l(S.T.P.) of acrolein/l of catalyst bed · h,
- 10 f) the second fixed-bed catalyst consists of a catalyst bed arranged in two spatially successive reaction zones C,D, the temperature of reaction zone C being from 230 to 270°C and the temperature of reaction zone D being from 250 to 300°C and at the same time at least 5°C above the temperature of reaction zone C,
- 15 g) the reaction gas starting mixture 2 flows first through reaction zone C and then through reaction zone D and
- h) the reaction zone C extends to an acrolein conversion of from 55 to 85 mol%.
- 20
2. A process as claimed in claim 1, wherein the reaction zone A extends to a propene conversion of from 50 to 70 mol%.
3. A process as claimed in claim 1, wherein the reaction zone A extends to a propene conversion of from 65 to 75 mol%.
- 25
4. A process as claimed in any of claims 1 to 3, wherein the reaction zone C extends to an acrolein conversion of from 65 to 80 mol%.
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5. A process as claimed in any of claims 1 to 4, wherein the temperature of the reaction zone B is at least 10°C above the temperature of the reaction zone A.
- 35
6. A process as claimed in any of claims 1 to 5, wherein the temperature of the reaction zone D is at least 20°C above the temperature of the reaction zone C.
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7. A process as claimed in any of claims 1 to 6, wherein the temperature of the reaction zone B is from 305 to 340°C.
8. A process as claimed in any of claims 1 to 6, wherein the temperature of the reaction zone B is from 310 to 330°C.
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9. A process as claimed in any of claims 1 to 8, wherein the temperature of the reaction zone C is from 245 to 260°C.

10. A process as claimed in any of claims 1 to 8, wherein the temperature of the reaction zone D is from 265 to 285°C.
- 5 11. A process as claimed in any of claims 1 to 10, wherein the propene conversion in a single pass in the first reaction stage is  $\geq 94$  mol%.
- 10 12. A process as claimed in any of claims 1 to 11, wherein the selectivity of the acrolein formation and of the acrylic acid byproduct formation together in a single pass in the first reaction stage is  $\geq 94$  mol%.
- 15 13. A process as claimed in any of claims 1 to 12, wherein the acrolein conversion in a single pass in the second reaction stage is  $\geq 94$  mol%.
- 20 14. A process as claimed in any of claims 1 to 13, wherein the selectivity of the acrylic acid formation balanced over both reaction stages is  $\geq 85$  mol%, based on propene converted.
- 25 15. A process as claimed in any of claims 1 to 14, wherein the propene loading of the first fixed-bed catalyst is  $\geq 165$  l(S.T.P.)/l · h.
- 30 16. A process as claimed in any of claims 1 to 15, wherein the propene loading of the first fixed-bed catalyst is  $\geq 170$  l(S.T.P.)/l · h.
- 35 17. A process as claimed in any of claims 1 to 16, wherein the at least one inert gas contained in the reaction gas starting mixture 1 comprises  $\geq 40\%$  by volume of molecular nitrogen.
- 40 18. A process as claimed in any of claims 1 to 16, wherein the at least one inert gas contained in the reaction gas starting mixture 1 comprises  $\geq 60\%$  by volume of molecular nitrogen.
- 45 19. A process as claimed in any of claims 1 to 18, wherein the at least one inert gas contained in the reaction gas starting mixture 1 comprises steam.
20. A process as claimed in any of claims 1 to 19, wherein the at least one inert gas contained in the reaction gas starting mixture 1 comprises CO<sub>2</sub> and/or CO.

21. A process as claimed in any of claims 1 to 20, wherein the propene content of the reaction gas starting mixture 1 is from 4 to 15% by volume.

5 22. A process as claimed in any of claims 1 to 21, wherein the active material of the first fixed-bed catalyst is at least one multimetal oxide of the formula I



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where

$\text{X}^1$  is nickel and/or cobalt,

15  $\text{X}^2$  is thallium, an alkali metal and/or an alkaline earth metal,

$\text{X}^3$  is zinc, phosphorus, arsenic, boron, antimony, tin, cerium, lead and/or tungsten,

$\text{X}^4$  is silicon, aluminum, titanium and/or zirconium,

20 a is from 0.5 to 5,

b is from 0.01 to 5,

c is from 0 to 10,

d is from 0 to 2,

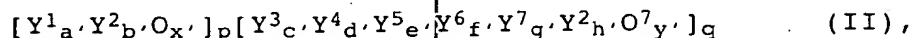
e is from 0 to 8,

25 f is from 0 to 10 and

n is a number which is determined by the valency and frequency of the elements other than oxygen in I.

23. A process as claimed in any of claims 1 to 21, wherein the active material of the first fixed-bed catalyst is at least one multimetal oxide of the formula II

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35 where

$\text{Y}^1$  is bismuth, tellurium, antimony, tin and/or copper,

$\text{Y}^2$  is molybdenum and/or tungsten,

$\text{Y}^3$  is an alkali metal, thallium and/or samarium,

40  $\text{Y}^4$  is an alkaline earth metal, nickel, cobalt, copper, manganese, zinc, tin, cadmium and/or mercury,

$\text{Y}^5$  is iron, chromium, cerium and/or vanadium,

$\text{Y}^6$  is phosphorus, arsenic, boron and/or antimony,

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$Y^7$  is a rare earth metal, titanium, zirconium, niobium, tantalum, rhenium, ruthenium, rhodium, silver, gold, aluminum, gallium, indium, silicon, germanium, lead, thorium and/or uranium,

5

$a'$  is from 0.01 to 8,

$b'$  is from 0.1 to 30,

$c'$  is from 0 to 4,

$d'$  is from 0 to 20,

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$e'$  is from 0 to 20,

$f'$  is from 0 to 6,

$g'$  is from 0 to 15,

$h'$  is from 8 to 16,

$x', y'$  are numbers which are determined by the valency and

15

frequency of the elements other than oxygen in II and

$p, q$  are numbers whose ratio  $p/q$  is from 0.1 to 10,

containing three-dimensional regions which are delimited from their local environment as a result of their composition differing from their local environment and have the chemical composition  $Y^1_a Y^2_b O_x$  and whose maximum diameters are from 1 nm to 100  $\mu m$ .

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24. A process as claimed in any of claims 1 to 23, wherein the first fixed-bed catalyst comprises annular and/or spherical catalysts.

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25. A process as claimed in claim 24, wherein the ring geometry is the following:

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external diameter: from 2 to 10 mm,

length: from 2 to 10 mm,

wall thickness: from 1 to 3 mm.

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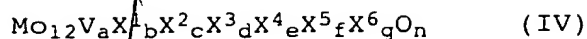
26. A process as claimed in claim 24, wherein the spherical catalyst is a coated catalyst consisting of a spherical support (from 1 to 8 mm diameter) and a coat of active material applied thereon (from 10 to 1000  $\mu m$  thick).

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27. The process as claimed in any of claims 1 to 26, wherein the first and the second reaction stages are each carried out in a two-zone tube-bundle reactor.

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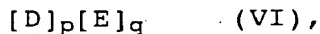
28. A process as claimed in any of claims 1 to 27, wherein the active material of the second fixed-bed catalyst is at least one multimetal oxide of the formula IV



5 where

- $\text{X}^1$  is W, Nb, Ta, Cr and/or Ce,  
 $\text{X}^2$  is Cu, Ni, Co, Fe, Mn and/or Zn,  
 $\text{X}^3$  is Sb and/or Bi,  
 10  $\text{X}^4$  is one or more alkali metals,  
 $\text{X}^5$  is one or more alkaline earth metals,  
 $\text{X}^6$  is Si, Al, Ti and/or Zr,  
 a is from 1 to 6,  
 b is from 0.2 to 4,  
 15 c is from 0.5 to 18,  
 d is from 0 to 40,  
 e is from 0 to 2,  
 f is from 0 to 4,  
 g is from 0 to 40 and  
 20 n is a number which is determined by the valency and frequency of the elements other than oxygen in IV.

29. A process as claimed in any of claims 1 to 27, wherein the active material of the second fixed-bed catalyst is at least  
 25 one multimetal oxide of the formula VI



where

- 30 D is  $\text{Mo}_{12}\text{V}_a\text{Z}^1_b\text{Z}^2_c\text{Z}^3_d\text{Z}^4_e\text{Z}^5_f\text{Z}^6_g\text{O}_x$  ,  
 E is  $\text{Z}^7_{12}\text{Cu}_h\text{H}_i\text{O}_y$  ,  
 $\text{Z}^1$  is W, Nb, Ta, Cr and/or Ce,  
 $\text{Z}^2$  is Cu, Ni, Co, Fe, Mn and/or Zn,  
 35  $\text{Z}^3$  is Sb and/or Bi,  
 $\text{Z}^4$  is Li, Na, K, Rb, Cs and/or H,  
 $\text{Z}^5$  is Mg, Co, Sr and/or Ba,  
 $\text{Z}^6$  is Si, Al, Ti and/or Zr,  
 $\text{Z}^7$  is Mo, W, V, Nb and/or Ta,  
 40  $a''$  is from 1 to 8,  
 $b''$  is from 0.2 to 5,  
 $c''$  is from 0 to 23,  
 $d''$  is from 0 to 50,  
 45  $e''$  is from 0 to 2,  
 $f''$  is from 0 to 5,

g" is from 0 to 50,

h" is from 4 to 30,

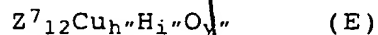
i" is from 0 to 20 and

x", y" are numbers which are determined by the valency and

5 frequency of the elements other than oxygen in VI and

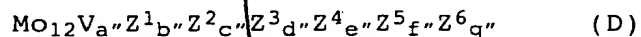
p, q are numbers other than zero whose ratio p/q is from  
160:1 to 1:1,

10 which is obtainable by separately preforming a multimetal  
oxide material (E)



in finely divided form (starting material 1) and then

15 incorporating the preformed solid starting material 1 into an  
aqueous solution, an aqueous suspension or a finely divided  
dry blend of sources of the elements Mo, V, Z<sup>1</sup>, Z<sup>2</sup>, Z<sup>3</sup>, Z<sup>4</sup>,  
Z<sup>5</sup>, Z<sup>6</sup>, which contains the abovementioned elements in the  
stoichiometry D



(starting material 2), in the desired ratio p:q, drying any  
25 resulting aqueous mixture, and calcining the dry precursor  
material thus obtained, before or after it has been dried, at  
from 250 to 600°C to give the desired catalyst geometry.

30. A process as claimed in any of claims 1 to 29, wherein the  
second fixed-bed catalyst comprises annular catalysts.

31. A process as claimed in any of claims 1 to 29, wherein the  
second fixed-bed catalyst comprises spherical catalysts.

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